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Dissociative Adsorption of H_2 on the H/Si(100) Surface

The Effect of Intradimer π-Bonding Disruption

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We have studied dissociative H_2 adsorption on the H/Si(100) surface by means of pseudopotential density functional theory calculations. This work is directly motivated by the observations of Biederman *et al.* [*Phys. Rev. Lett*., **83**, 1810 (1999)]: "H_2 adsorption is significantly promoted in an interdimer configuration of two adjacent singly occupied dimers." We find that there is no adsorption barrier on the local site where two quasi-free dangling bonds are available; the adsorption energy is estimated to be 2.6 eV per H_2 within the local density approximation. We present maximally localized Wannier functions that clearly illustrate the behavior of dangling orbitals upon the approach of H_2. The results suggest that intradimer π-bonding disruption is crucial for the significant promotion of H_2 adsorption on Si(100).
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Hydrogen adsorption on silicon surfaces has been a subject of great technological and theoretical interest for many years. Because of its relative simplicity, the system is regarded as a prototype for studying the interaction of gas molecules with covalent surfaces. In addition, a better understanding of the adsorption process is necessitated in semiconductor manufacturing, *e.g.*, epitaxial film growth of Si. The structural and electronic properties of H/Si(100) have been resolved to a great extent over the past decades. However the details of dynamic phenomena such as dissociative adsorption of hydrogen molecules are still ambiguous.[1]

The extremely low sticking coefficient at room temperature is a well known character of the dissociative H_2 adsorption,[2-4] indicating the presence of a substantial barrier. In accordance with the principle of adsorption-desorption reversibility, associative desorption should experience the same energy barrier as well. However, no significant barrier has been found; Kolasinski *et al.*[5] demonstrated that there was no sizable potential drop in the course of desorption. Note that the adsorption-desorption reciprocity is basically deduced from a hypothesis that there is a unique pathway for the dynamic process. In this way, the adsorption energetics solely depends on the state of incoming hydrogen molecules. However, the H_2 sticking probability also appears to be a strong function of surface temperature.[2-4] The observation implies that the motion of the surface atoms may play an important role, so-called phonon-assisted sticking.[2,3] In other words, heating the surface generates certain atomic configurations that result in low adsorption energy barriers.[6,7]

It is evident that the adsorption energetics is determined by the interplay between the geometric and the electronic structures. In fact these two properties tend to go hand in hand; that is, altering a local atomic configuration brings about a change in corresponding electronic states, and vice versa. Recently, Biedermann *et al.*[8] reported that the H_2 adsorption was significantly promoted in an interdimer configuration of adjacent singly occupied dimers even at room temperature. They estimated that the H_2 sticking probability on the active site increased by approximately ten orders of magnitude over that on a clean surface. Such dramatic reactivity enhancement was accounted for by the availability of quasi-free dangling bonds;[8] that is, singly occupied dimers render dangling bonds free to react by virtue of π-bonding disruption. At present, however, it is somewhat unclear how π-bonding disruption contributes to the promotion of H_2 adsorption. Answering this question may also shed some light on the underlying reasons for the strong surface temperature dependence of the H_2 adsorption on Si(100).

In this paper we present a reaction pathway and energetics of dissociative H_2 adsorption on a local site where two adjacent dimers are singly occupied by H atoms in a *cis* position. Maximally localized Wannier functions demonstrate how the remaining quasi-free dangling bonds respond to an incoming H_2 molecule. We also discuss the effect of surface temperature in connection with possible π-bonding disruption caused by thermally induced dimer stretching and/or twisting.

Calculation

All calculations presented in this paper have been performed within the framework of the Car-Parrinello approach [Car-Parrinello molecular dynamics (CPMD)].[9,10] The silicon surface is modeled by a (4×4) surface unit cell, as shown in Fig. 1, periodically repeated with five atomic layers and about 10 Å vacuum space over the surface. The bottom layer silicon atoms are fixed at the bulk position and every dangling bond is passivated by a hydrogen atoms. Ion-electron interactions are described by using a norm-conserving pseudopotential[11] and electron correlations are taken into account by the Ceperley-Alder form[12] parameterized by Perdew and Zunger.[13] We use the plane-wave cutoff energy (E_{cut}) of $10\,Ry$; a convergence test shows that $E_{cut} = 10\,Ry$ is sufficient for obtaining optimal structures and adsorption energies with reasonable accuracy. For the k point sampling of the Brillouin zone (BZ), only the gamma (Γ) point is used because of the large size of supercell considered here.

Results and Discussion

First we have looked into a change in surface configuration by occupying dangling bonds with H atoms. Figure 1 shows surface structures considered in this work; (a) the $p(2 \times 2)$-type clean surface where dimers are alternatively buckled, (b) H atoms adsorb on two inner dimers in a *cis* configuration, and (c) all dangling bonds of the inner dimers are saturated by H atoms. These structures are optimized by fully relaxing the topmost four atomic layers until all residual forces become smaller than 5×10^{-4} Hartree/Bohr within the local density approximation (LDA). The alternatively buckled configuration has been known as a ground state of Si(100), resulting in the $p(2 \times 2)$ or the $c(4 \times 2)$ symmetry; the buckled dimers may undergo thermal fluctuations at the energy expense of about 0.1 eV.[14] The buckling angle of 17.6° and the dimer length of 2.30 Å are in excellent agreement with previous LDA slab calculations[15,16] in which the bond lengths and the buckling angles range from 2.29 to

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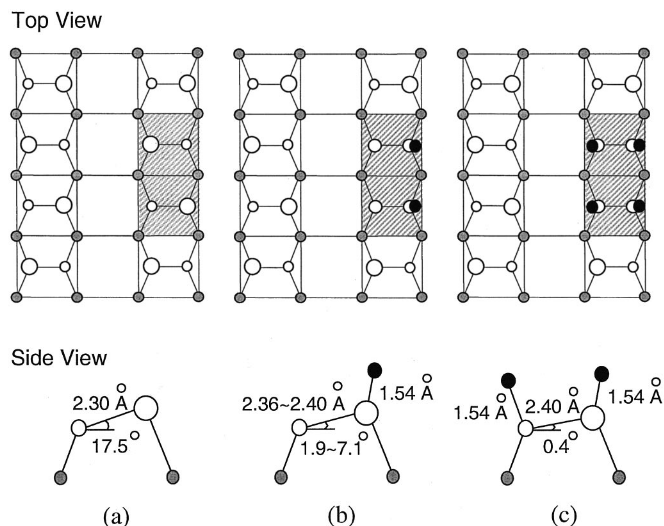

Figure 1. Top and side views of the two topmost atomic layers of surface structures considered in this study: (a) the p(2 × 2)-type clean surface, (b) two inner dimers are singly occupied by H atoms, (c) two inner dimers are fully saturated. Only side views of hatched areas are displayed, together with buckling angle, dimer bond length, and H-Si bond length. Note the variation of buckling angle and dimer bond length in case (b) is attributed to a difference in the buckling nature of adjacent outer dimers. Big and small open circles represent the up and the down atoms of buckled dimers, respectively, and the H atoms and the second layer Si atoms are indicated by small black and gray circles, respectively.

2.33 Å and from 17° to 19°, respectively. As shown in Fig. 1b, the adsorption of H atoms on the inner dimers substantially weakens the dimer buckling. The buckling angles of 1.9°-7.1° are quite comparable with 2°-4° as obtained by Vittadini *et al.*[17] The slight difference is primarily attributed to the buckling of the adjacent outer dimers included in our model. Saturating both dangling bonds of the inner dimers (Fig. 1c) merely alters the bond lengths compared to case (b), but the buckling virtually disappears.

Figure 2a shows the optimum reaction path of the dissociative H_2 adsorption in terms of the H-H distance ($d_{H\text{-}H}$) and the height of the H_2 center of mass above the active site (Z_H). In this search, we use a procedure with three steps: (*i*) optimize z and x positions of two H atoms for a fixed y coordinate, (*ii*) allow y positions to move while holding the H-H distance constant at a given value, and (*iii*) for the constrained H-H distance, all coordinates are allowed to move until all residual forces fall below 5×10^{-4} Hartree/Bohr. From these calculations, we can obtain optimal positions of the H atoms and the surface atoms for a certain H-H distance. The surface atoms are only allowed to relax in the course of step (*iii*). The surface relaxation plays an insignificant role in determining the reaction path; recall that there is a mere variation in the surface configuration during the adsorption process. The insets show the atomic configuration of the incoming H_2 and the surface atoms displaced near the active site. Here four selected points on the reaction path A, B, C, and D are ($d_{H\text{-}H}$, Z_H) = (0.83, 2.87), (1.03, 1.37), (2.33, 1.18), and (3.84, 1.44), respectively. The total energy along the reaction path, as shown in Fig. 2b, demonstrates that the H_2 molecule dissociates directly into the most stable final state, *i.e.*, there is no activation energy barrier. The adsorption energy is estimated to be 2.6 eV per H_2 molecule from the local density approximation-density functional theory (LDA-DFT) calculation. Such barrier-free adsorption evidently originates from quasi-free dangling orbitals available on the active site. Recall that the extremely low sticking probability of H_2 on the clean Si(100) surface is primarily attributed to rather strong mutual interactions of dangling bonds. We can also find low barrier or barrier-free dissociative H_2 adsorption in the case of metal surfaces where electronic states spread spatially and thus efficiently interact with incoming H_2 molecules.[18,19]

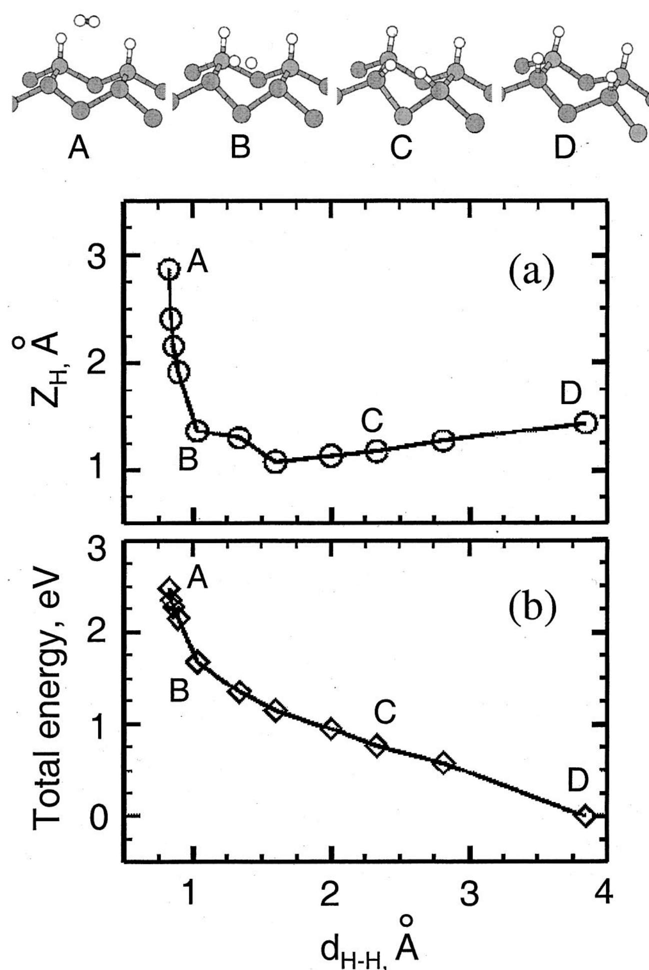

Figure 2. (a) The optimal reaction path of the dissocative H_2 adsorption in terms of the H-H distance ($d_{H\text{-}H}$) and the distance between the H_2 center of mass and the averaged height of the active Si surface atoms (Z_H). (b) The total energy variation along the reaction path, represented as a function of $d_{H\text{-}H}$. The insets illustrate the atomic configuration of the incoming H_2 and the surface atoms displaced near the active site for four selected points A, B, C, and D, as indicated. Small white circles and bigger gray circles indicate the H atoms and the Si atoms, respectively.

Figure 3 shows the isosurface densities of maximally localized Wannier functions[20] for dangling bonds (a) before and (b) after the introduction of H_2 to near the active site. The H-H Wannier function is also displayed in case b. Prior to H_2 introduction, as shown in Fig. 3a, two dangling orbitals are weakly coupled through the sublayer. When the H_2 molecule approaches the active site, however, these orbitals appear to smear out and thus interact efficiently with the incoming H_2 molecule (Fig. 3b). As illustrated here, Wannier functions are likely to be sufficent to provide useful information about the interaction between an incoming H_2 molecule and the quasi-free dangling bonds.

This study leads us to speculation that the anomalous temperature dependence of the H_2 adsorption on Si(100) may be directly linked to intradimer π-bonding disruption. Raising the surface temperature is inevitably accompanied by lattice thermal motions. At moderate temperatures, in most cases dimers may undergo fluctuations while preserving the π-bonding interaction. As the surface temperature is increased, however, the movement of surface atoms will be radical; that is, thermally induced dimer twisting and stretch-

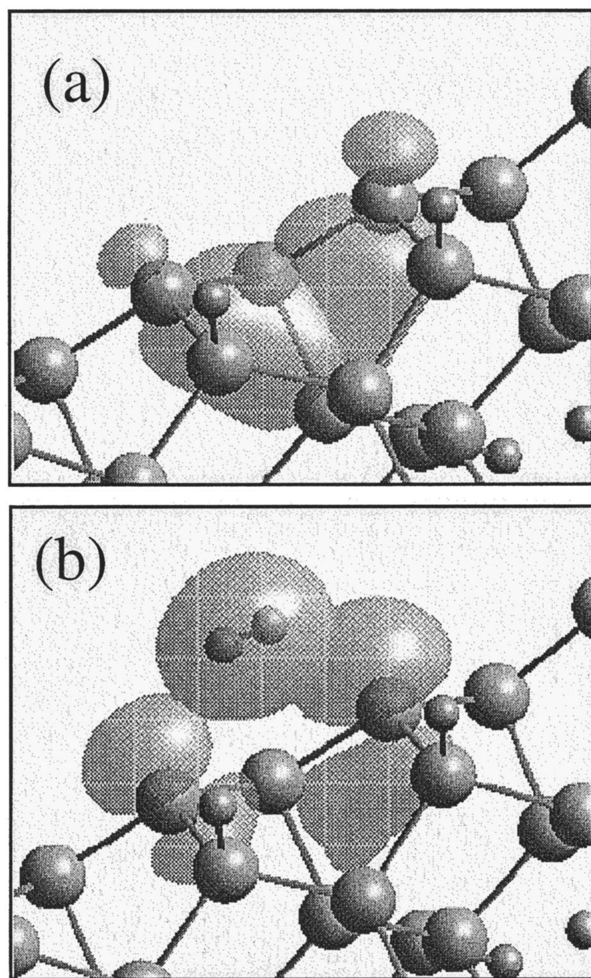

Figure 3. Maximally localized Wannier functions of dangling orbitals on the active site where two adjacent dimers are singly occupied by H atoms, for the Γ-point approximation;[20] (a) before H_2 introduction, (b) upon the approach of H_2, together with the H_2 Wannier function. Small and big gray balls represent the H atoms and the Si atoms, respectively.

ing modes become stronger. As a result the mutual interaction between dimer dangling bonds gets weaker which in turn renders dangling bonds more reactive. In other words, higher substrate temperatures provide more chances of encountering quasi-free dangling orbitals to incoming H_2 molecules. Although dimer flipping also brings about a certain configuration that may lower adsorption barrier to a degree,[6] the structural effect could be insignificant given that Si(111) 7×7 and Si(100) 2×1 surfaces show similar surface temperature dependence.[3] In view of this, it would be reasonable to claim that the dissociative H_2 adsorption is primarily dependent on the availability of quasi-free dangling bonds on a local surface on which the H_2 molecule impinges. This argument could also be supported by recent experiments that demonstrate a significant promotion of H_2 adsorption on vicinal Si(001) surfaces where quasi-free dangling orbitals are commonly available due to severe lattice deformation.[21,22]

Conclusions

In this paper, we have presented a DFT study of dissociative H_2 adsorption on a local Si(100) surface where two adjacent dimers are singly occupied by H atoms in a *cis* configuration. This work demonstrates that there is no energy barrier to the H_2 adsorption; the adsorption energy is estimated to be 2.6 eV per H_2 in the local density approximation. Maximally localized Wannier functions illustrate that quasi-free dangling orbitals available on the active site are weakly coupled through the sublayer prior to H_2 introduction. Upon the H_2 approach, however, they appear to smear out and thus interact efficiently with the H_2 orbitals. This study suggests that the anomalously strong surface temperature dependence of dissociative H_2 adsorption on Si(100) could be directly linked to intradimer π-bonding disruption caused by thermally induced dynamical distortion of Si surface atoms.

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References

1. K. Oura, V. G. Lifshits, A. A. Saranin, A. V. Zotov, and M. Katayama, *Surf. Sci. Rep.,* **35**, 1 (1999).
2. U. Höfer, *Appl. Phys. A: Solids Surf.,* **63**, 533 (1996).
3. P. Bratu, W. Brenig, A. Groß, M. Hartmann, U. Höfer, P. Kratzer, and R. Russ, *Phys. Rev. B,* **54**, 5978 (1996).
4. P. Bratu, K. L. Kompa, and U. Höfer, *Chem. Phys. Lett.,* **251**, 1 (1996).
5. K. W. Kolasinski, W. Nessler, A. de Meijere, and E. Hasselbrink, *Phys. Rev. Lett.,* **72**, 1356 (1994).
6. P. Kratzer, B. Hammer, and J. K. Nørskov, *Chem. Phys. Lett.,* **229**, 645 (1994).
7. E. Pehlke and M. Scheffler, *Phys. Rev. Lett.,* **74**, 952 (1995).
8. A. Biedermann, E. Knoesel, Z. Hu, and T. F. Heinz, *Phys. Rev. Lett.,* **83**, 1810 (1999).
9. R. Car and M. Parrinello, *Phys. Rev. Lett.,* **55**, 2471 (1985).
10. J. Hutter, A. Alavi, T. Deutch, M. Bernasconi, S. Goedecker, D. Marx, M. Tuckerman, and M. Parrinello, *CPMD*, Max-Planck Institute für Festköerperforschung, Germany, and IBM-Zurich Research Laboratory, Zurich, Switzerland (1995-1999).
11. N. Troullier and J. L. Martins, *Phys. Rev. B,* **43**, 1993 (1991).
12. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.,* **45**, 566 (1980).
13. J. Perdew and A. Zunger, *Phys. Rev. B,* **23**, 5048 (1981).
14. G. S. Hwang, *Surf. Sci.,* **465**, L789 (2000).
15. J. E. Northrup, *Phys. Rev. B,* **47**, 10032 (1993).
16. J. Fritsch and P. Pavone, *Surf. Sci.,* **344**, 159 (1995).
17. A. Vittadini, A. Selloni, and M. Casarin, *Phys. Rev. B,* **49**, 11191 (1994).
18. J. K. Nørskov, A. Houmöller, P. Johansson, and B. I. Lundqvist, *Phys. Rev. Lett.,* **46**, 257 (1981).
19. B. Hammer, K. W. Jacobsen, and J. K. Nørskov, *Phys. Rev. Lett.,* **70**, 1971 (1992).
20. P. L. Silvestrelli, N. Marzari, D. Vanderbilt, and M. Parrinello, *Solid State Commun.,* **107**, 7 (1998).
21. P. Kratzer, E. Pelhlke, and M. Scheffler, *Phys. Rev. Lett.,* **81**, 5596 (1998).
22. M. Dürr, M. B. Raschke, and U. Höfer, *J. Chem. Phys.,* **111**, 10411 (1999).